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Pulsed Raman Measurement of the Onset of Recrystallization in Laser Annealing

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ABSTRACT

We have made the first time-resolved measurement of the onset of recrystallization following pulsed laser irradiation of ion-implanted silicon. We find recrystallization to be nearly complete 25 nsec after a 7 nsec annealing pulse with focussed energy density of  $0.6 \text{ J/cm}^2$ ...

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Pulsed laser and electron beam annealing of ion-implantation-produced damage has yielded remarkably high quality doped semiconductor material - particularly in the case of silicon. Laser annealed specimens have been thoroughly studied with a great variety of probes, 1,2,3 usually hours to days after the pulsed anneal and the results used to construct scenarios of the pulsed anneal process itself. However, there is a distinct lack of direct data on conditions prevailing in the semiconductor during the anneal process and hence also considerable uncertainty on the regrowth mechanisms responsible for such high quality material. A notable exception is the use of time-resolved reflectivity by Auston, et al and subsequently by several other groups. In addition we recently demonstrated that Raman scattering can be used with nanosecond time resolution to probe the temperature of laser-heated crystalline silicon. We report here the first time-resolved Raman measurements of the onset of recrystallization in laser-irradiated, ion-implantation-amorphized silicon.

The experimental apparatus is very similar to that described previously for the time-resolved Raman measurements on crystalline silicon. Important differences were the following: 1) a 2.55 meter confocal spherical-mirror delay line was used to obtain adjustable delays for the probe pulse at 406.5 nm; 2) a computer-controlled x-y scanning stage was used to raster-scan the sample to present virgin unannealed surface to each successive laser pulse; 3) a PARC OMA-2 vidicon was used at the output of the Spex 1401 spectrometer for signal detection. A PDP 11/34 computer controlled the vidicon as well as the sample scanning stage. The OMA-2 was cooled to dry ice temperature and signal was typically integrated for 10 minutes. During readout 10 adjacent channels were integrated before digitizing and then sent to the computer for storage and background subtraction. The effective detector resolution was therefore 250 µm; however, the image size of ~700 µm at the entrance slit was the

resolution-limiting factor. To reduce stray light the intermediate slit was typically operated at 1000 to 1500  $\mu m$ .

The ion-implanted silicon samples were obtained from Spire Corporation implanted with 200 keV arsenic to a dose of  $10^{15}/\text{cm}^2$ . The projected range of 200 keV arsenic is 0.11 µm<sup>7</sup> with heavy damage extending somewhat further. A probe pulse at 406.5 nm has an absorption length in room temperature crystalline silicon of ~0.16 µm and since the Raman light is absorbed on the way out at nearly the same rate, the effective probe depth is ~0.08 µm. Higher crystalline temperatures will reduce this depth still further. Thus even if recrystallization has proceeded through to the undamaged substrate, the probe pulse will sample only material originally amorphized by ion-implantation. Note if any amorphous silicon remains under the recrystallized material the probe light is even more strongly absorbed in it, thus preventing any sampling of undamaged substrate.

The heat/probe technique used a two-beam configuration with an intense annealing beam and a weak, délayed probe beam. In addition the probe was focussed to a diameter at half power points approximately 1/3 to 1/2 that of the annealing beam which was typically 200 µm. Spot overlap was repeatedly checked with a 50 µm pinhole placed at the exact position of the silicon sample. The use of a probe beam also allowed us to select a shorter wavelength ( $\lambda_{\rm p} = 406.5$  nm) which is more strongly absorbed in crystalline silicon ( $\tau = 6 \times 10^4$  cm<sup>-1</sup>) than the annealing laser wavelength ( $\lambda_{\rm H} \approx 485$  nm) where  $\alpha = 1.2 \times 10^4$  cm<sup>-1</sup>. A Molectron UV-1000 pulsed nitrogen laser operating at 15 Hz was used to excite simultaneously the two dye lasers. Maximum power for the annealing pulse was obtained from a proad-band dye laser ( $\Delta \lambda \approx 10$  nm) with no dispersive element in the cavity while the probe pulse was obtained from a Molectron DL-200 dye laser. Note that if some probe light overlaps with the weak fringes of the anneal pulse spot no Raman signal will arise from

these regions if no recrystallization has occurred since the spectrum of amorphous silicion is weaker by greater than a factor of 100 in the region of 500 cm<sup>-1</sup>.

The only evidence presented thus far of the time scale on which recrystallization occurs after pulsed laser irradiation is quite indirect. It consists of timing the fall of the reflectivity enhancement and <u>assuming</u> that the high reflectivity is due to molten silicon. As shown in reference 6 the Raman evidence shows this assumption to be incorrect. However, we now show that Raman scattering does allow one to measure and time-resolve the recrystallization rate rather directly.

The onset of recrystallization in the ion-implanted amorphized silicon samples was studied using a variety of time delays with the optical delay line. Figure 1 displays Raman signals obtained with an annealing pulse power density of 0.6 J/cm<sup>2</sup> in the central 50 µm and at probe delays of 28 nsec, 59 nsec, 212 nsec, and one spectrum taken with the heat beam off. One clearly sees the growth of the Raman signal is very rapid. The crystalline signal is essentially full size at 59 nsec and a sizeable signal occurs already at 28 nsec. For comparison we display in the inset the shape of the reflectivity rise observed in this material with a CW 514.5 nm beam focussed to ~40 µm diameter at the center of the pulsed beams. The lower trace of the inset shows the two pulsed beams indicating that for some of the duration of the probe pulse at 28 nsec the sample is still in an enhanced reflectivity state.

To examine less ambiguously whether a crystalline signal exists during the high reflectivity phase, we repeated the 28 nsec measurement using a power density of 0.9 J/cm² for the heating pulse. This produced a high reflectivity phase lasting 60 nsec followed by a >25 nsec tail.

Amplitude stability of the annealing pulse was ±5% and the reflectivity duration varied by less than ±20ns during data acquisition. The Raman signal was

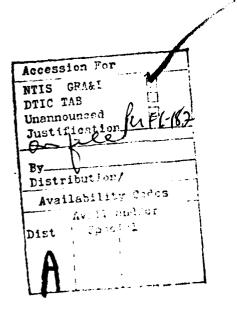
clearly present at a level of  $\sim 500$  counts in 5 minutes. During the high reflectivity phase the reflectivity rises from  $\sim 35\%$  to  $\sim 60\%$ . Since this affects the transmission of scattered light through the surface as well as the laser light, one expects a decrease of  $(\frac{.4}{.65})^2 = .38$  in the Raman signal. This factor accounts essentially for all of the drop in signal observed at 28 nsec. Thus we conclude that recrystallization is far advanced already at 28 nsec even though the sample is still in a high reflectivity phase.

The quality of the recrystallized material produced either at 0.6 J/cm<sup>2</sup> or at 0.9 J/cm<sup>2</sup> was studied by using the same 514.5 nm argon laser beam that was used for the reflectivity signature. The strength of the Raman signal was essentially identical to that obtained from an unimplanted edge of the wafer. This shows that recrystallization has occurred throughout the depth of the implantation-produced amorphization. (Recall amorphous silicon has no sharp Raman signature and at 514.5 nm absorbs approximately 10 times as strongly as crystalline silicon.) Furthermore a simple CW Raman polarization study shows that in the central 40 µm region probed by the argon laser the recrystallized material has the same orientation as the substrate. Thus regrowth has apparently occurred epitaxially - it is not polycrystalline.

The ability to obtain a clear Raman signal during the high reflectivity phase destroys the validity of assuming the reflectivity is a signature of molten silicon. This result together with the Raman temperature measurement previously reported completely contradict thermal melting models 3,8 of the anneal process - viz. that the laser pulse induces normal thermal melting of the damaged lattice and that single crystal material is formed as the solid-liquid phase boundary moves to the surface. We believe that any realistic model of pulsed laser or electron-beam annealing will have to recognize the role of the dense solid state plasma created by the radiation pulse. In this respect the plasma annealing model proposed by Van Vechten,

et al<sup>9</sup> is a plausible first step. Also it will be very important to understand the mechanisms by which the normally rapid ( $\sim 10^{+12}/\text{sec}$ )<sup>10</sup> electron-lattice relaxation rates are inhibited<sup>11</sup> in the high carrier density regimes present during pulsed annealing.

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## Figure Caption

Figure 1. Stokes Raman spectrum of ion-implanted silicon obtained for several delays of the 406.5 nm probe pulse. For clarity, successive traces are vertically displaced by 500 counts. The lowest trace is for probe pulse only. Dispersion is 8 cm<sup>-1</sup>/channel, vidicon integration time was 5 minutes. Insets show reflectivity at 514 nm and pulse timing at 28 nsec.

